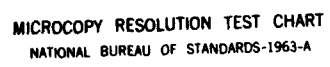


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Photothermal Analysis of Thin Films

by

**H. Coufal
P. Hefferle**

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Photothermal Analysis of Thin Films

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Abstract

Applications of photothermal depth profiling are described. Most recent results demonstrate the use of thermal delay lines and multiplex techniques.

1. Introduction

The photothermal effect can be observed whenever pulsed or modulated radiation is absorbed in a sample [1]. The sample under study is excited by the irradiation. Subsequent radiationless deexcitation causes local heating. If the lifetime of the excited states is short compared to the period of the excitation pulsed or modulated heat sources are generated giving rise to thermal waves. These thermal waves are critically damped, diffusive waves, i.e., within one wave length, the so called thermal diffusion length μ , the amplitude is attenuated by $e^{-2\pi}$. Therefore only heat generated within the diffusion length from the surface of a sample can contribute towards the temperature increase observed at this surface. These temperature waves can be readily detected at the surface using pyroelectric calorimeters [2] or other thermal or acoustic detectors [1]. At a modulation frequency f of 1 MHz thermal waves have typically a diffusion length of 1 μm . The thermal diffusion length is, however, frequency dependent $\mu \propto f^{-1/2}$. At very high modulation frequencies, therefore, only a very thin surface layer is seen in the photothermal signal. At slightly lower frequencies the same surface layer and heat from the adjacent layer reach the surface. The contribution by the additional layer can be determined if both layers are very thin by subtracting the signals at the two modulation frequencies. If the modulation frequencies differ substantially signals have to be corrected for the different amount of energy deposited during one excitation cycle. If the thickness of the individual layers is not negligible, a quantitative depth profile can not be readily reconstructed from frequency domain photothermal data, due to attenuation and dispersion of the thermal waves. Qualitative data, however, allow insight into the properties of samples. Two particularly interesting structures are discussed in the following paragraphs.

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2. Phase Shifter

The interpretation of photothermal spectra is complicated due to the involvement of thermal and possibly also acoustic properties in the signal generation process. Considerable effort was, therefore, spent to compare optical features of otherwise identical samples [1] or to use reference samples with well defined and optimized optical and thermal properties [3]. Comparing two signals requires either a dual beam arrangement for real time recording of sample and reference spectra, which is crucial for compensation techniques, or the subsequent recording of these spectra with an off line normalization. For applications requiring utmost sensitivity such as weakly absorbing samples [2,4] only the real time technique is suitable. For this type of sample there is, however, another alternative: weakly absorbing sample and well defined reference can be optically in series, the excitation being therefore simultaneous. If sample and reference are separated by a thermal delay line or a phaseshifter the detection can be sequential. Only one detector and subsequent electronics are required in this set up, such eliminating noise sources and reducing cost considerably.

Assuming excitation of the composite sample from the front side and detection of the thermal wave at the back side of the reference sample, for example by a pyroelectric calorimeter, following modes of thermal wave propagation are of interest:

At low modulation frequencies the thermal wave from the sample reaches the detector unattenuated, but slightly later than the reference wave. By in-phase and out-of-phase detection the signal components could be separated and then the ratio of both signals determined. The same result can be conveniently obtained by recording the phase angle of the composite signal. Being a photothermal spectrum this spectrum is a convolution of the true absorption spectrum of the sample under study and the yield for radiationless deexcitation.

At high enough a modulation frequency the thermal wave from the sample does not at all reach the detector. The photothermal signal of the reference sample is then caused only by the light transmitted through the sample and allows the detection of the true transmission spectrum of the sample. The absorption spectrum of the sample can then be determined readily. By ratioing the above phase angle spectrum with the true absorption spectrum the quantum yield for radiationless deexcitation can be determined.

To demonstrate this concept a pyroelectric calorimeter with a silver electrode was coated with a 0.1 mm thick transparent PMMA film. The silver film serves as reference sample, the PMMA film as phase shifter. On top of this phase shifter a 1 μm thick PMMA film doped with 0.8×10^{15} Nd_2O_3 was deposited as sample. The phase angle spectrum recorded at 2 Hz modulation frequency is shown in Fig. 1. It is in excellent agreement with spectra of identical samples obtained with much more sophisticated instrumentation [2]. By comparison with an absorption spectrum recorded with the same sample at 88 Hz modulation frequency the quantum yield for radiation less deexcitation was determined to be $90 \pm 5\%$ throughout the entire spectrum.

3. Multiplex Excitation

In the above example each modulation frequency had been excited and recorded separately. It would be convenient in this case and absolutely necessary for full depth profiling, which requires a complete modulation frequency spectrum to modulate and detect at many frequencies simultaneously. This has been done in photothermal spectroscopy in the wave length domain [6,7] and in photothermal imaging in the spatial domain [8,9]. This concept can be extended to the frequency domain, using Fourier transformations to obtain the information of interest. To generate as much intensity at

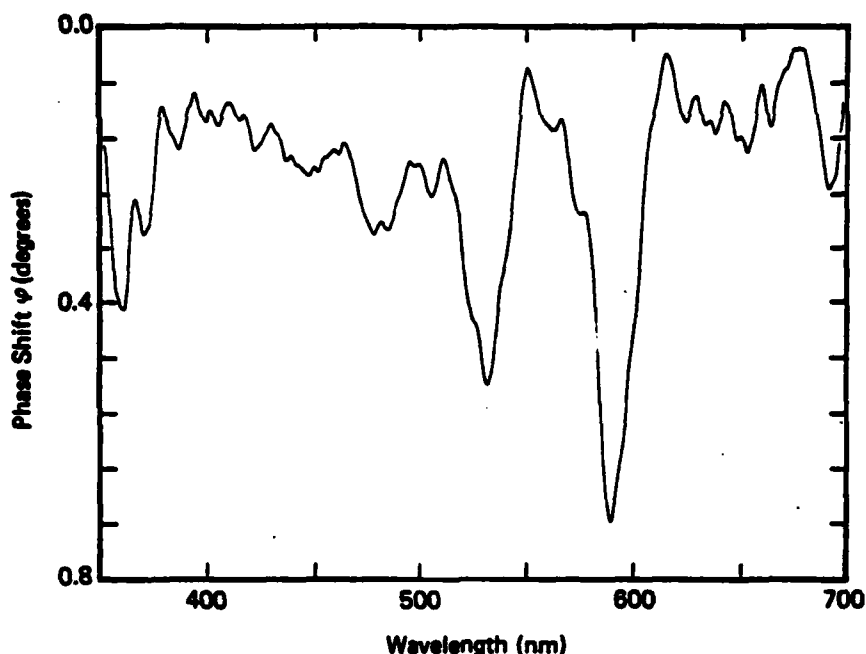


Fig. 1: Phase angle spectrum of 0.8×10^{15} Nd_2O_3 molecules in a $1 \mu\text{m}$ thick PMMA film coated on top of a 0.1 mm thick undoped PMMA film on a silver substrate. Recorded at 2.2 Hz modulation frequency.

high Fourier components as possible the otherwise stable output of a 6 mW HeNe-laser was modulated with white noise. Figure 2 shows the light intensity incident on the sample in the time domain. A thin film of homogeneously carbon doped PMMA generates the response of Fig. 3. By ratioing response and excitation the frequency dependence of the photothermal signal can be determined over the complete modulation frequency spectrum (Fig. 4). Data acquisition and Fourier transformation of the data required only 2.6 seconds. The frequency dependence determined with this technique is identical to the one determined conventionally one frequency at a time in more than 200 seconds. Both show clearly by their f^{-1} -frequency dependence that the sample was homogeneously doped [1]. Figure 5 shows clearly the frequency dependence of a thick sample obtained with the same technique.

4. Conclusion

It has been demonstrated that the photothermal analysis of thin films has a unique potential. Even without being able to construct an actual depth profile from photothermal data, mainly due to mathematical problems, valuable insight into the properties of the sample can be gained. In one example the known structure and thermal properties of a composite sample were used to obtain a spectrum of a thin surface layer with an amount of Nd^{3+} -ions corresponding to one monolayer. Furthermore the quantum yield for radiationless decay was obtained. In a second example with well defined optical and overall thermal properties the homogeneity of the doping was proven taking advantage of multiplex excitation.

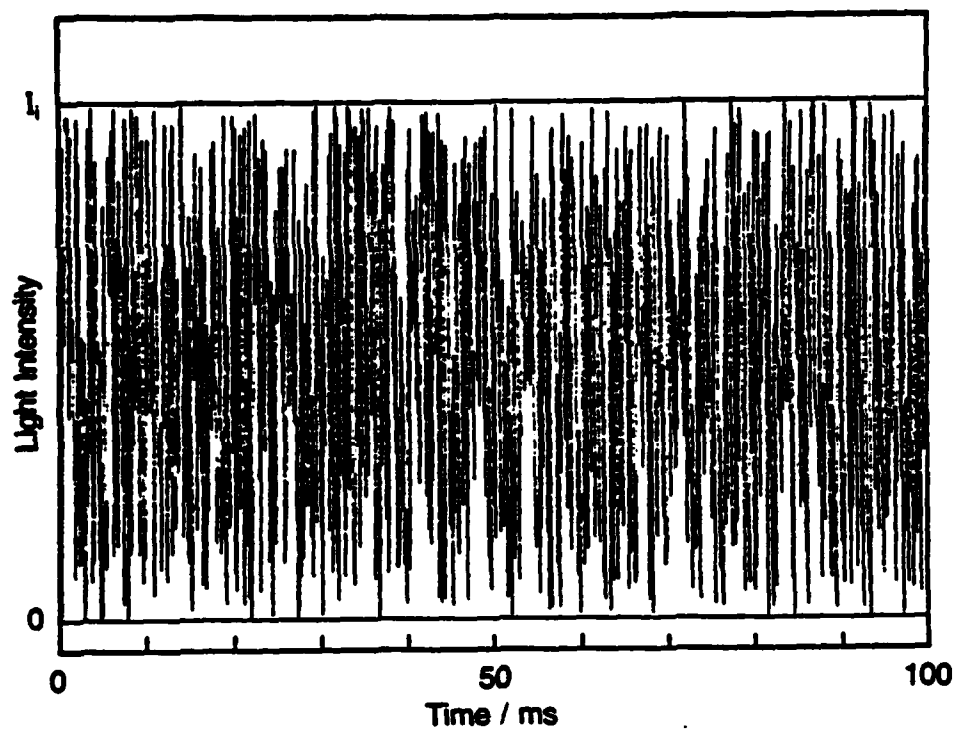


Fig. 2: Incident light intensity obtained by modulating CW laser with white noise.

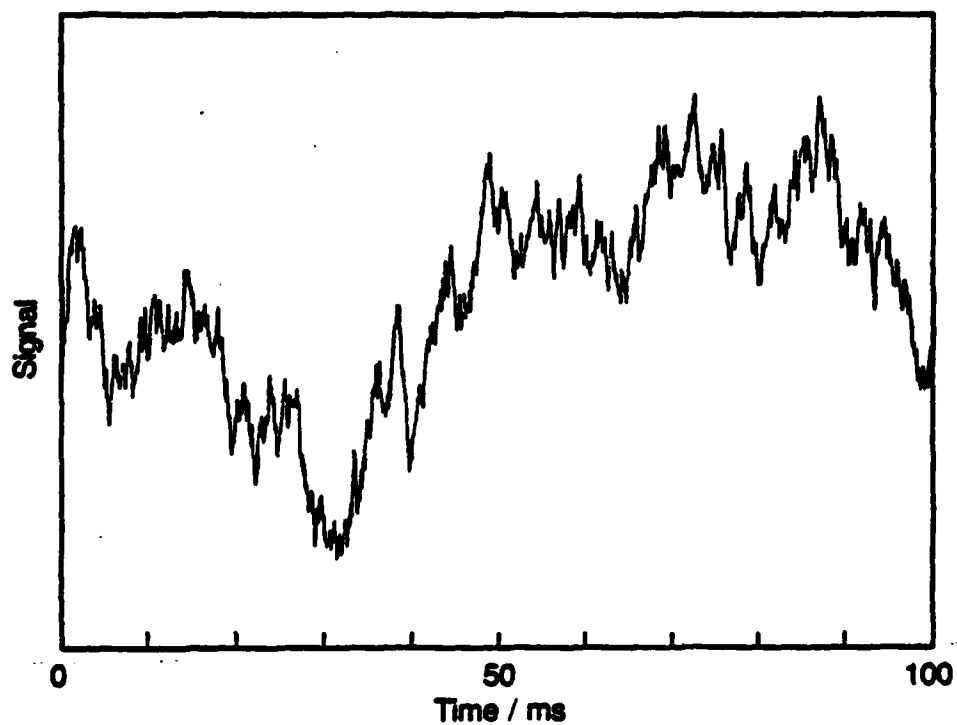


Fig. 3: Photothermal signal observed from a sample excited with the light intensity of Fig. 2.

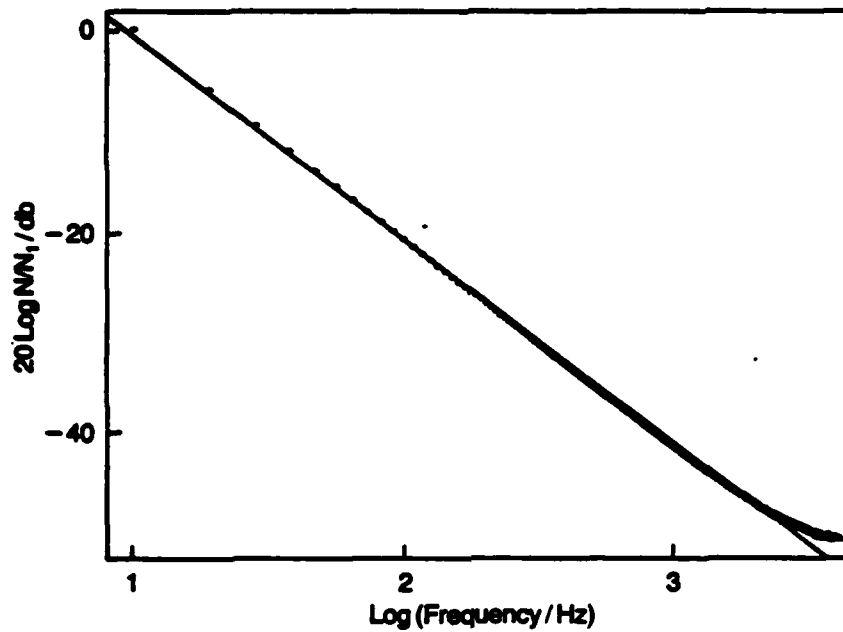


Fig. 4: Frequency dependence of the photothermal signal of a homogeneous, thin sample obtained by ratioing the Fourier transforms of Figs. 2 and 3.

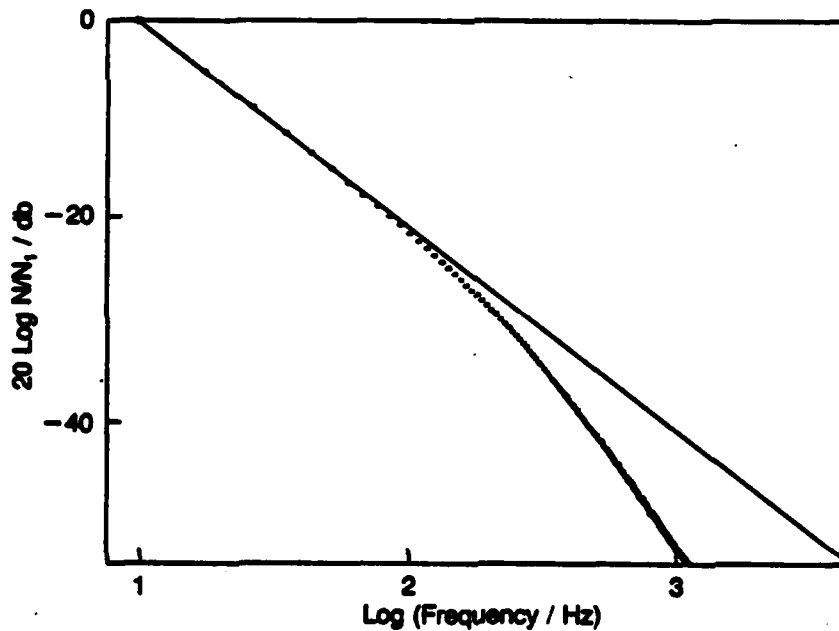


Fig. 5: Frequency dependence of the photothermal signal of a homogeneous, thick sample obtained by Fourier transform techniques.

5. Acknowledgments

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